High Efficiency and High Rate Deposited Amorphous Silicon-Based Solar Cells

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Fine-Grained Nanocrystalline Silicon p-Layer for High-Voc a-Si:H Solar Cells

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Abstract

Amorphous silicon (a-Si:H) single-junction solar cells with high open circuit voltage (Voc), up to 1.04 V, are routinely fabricated at the University of Toledo (UT) using a wide bandgap boron doped Si:H p-layer deposited at high hydrogen dilution and low substrate temperature and with a seed layer that promotes nanocrystalline silicon (nc-Si:H) formation.
It is important to understand the exact nanostructure of the p-type material used at UT and other laboratories to produce high-Voc solar cells. In an earlier paper, we reported our preliminary finding that these p-type materials used in UT's high-Voc solar cells are fine-grained nc-Si:H, based on a modeling study using AMPS. In this paper, we report our further investigation of the nanostructure of this p-type material using High Resolution Transmission Electron Microscope (HRTEM), which allows us to directly measure the nanostructure of the films, ~15nm thick, deposited on a-Si substrates. It is found from the HRTEM studies that the p-layer used at UT to obtain high-Voc a-Si solar cells is a mixed-phase material that contains fine-grained nc-Si:H embedded in an a-Si:H matrix. It is further concluded that the mixed phase p-layer with a higher volume fraction of nc-Si:H phase, within the range studied, leads to a higher V_{oc}. The optimum p-layer material for nip-type a-Si:H solar cells is neither at the onset of the transition between amorphous to (amorphous and nanocrystalline) mixed phase nor a nanocrystalline/microcrystalline material with a high volume fraction of crystalline phase.

Introduction

Amorphous silicon (a-Si:H) single-junction solar cells with high open circuit voltage (Voc), up to 1.04 V, are routinely fabricated at the University of Toledo (UT) using a wide bandgap boron doped Si:H p-layer deposited at high hydrogen dilution and low substrate temperature and with a seed layer that promotes nanocrystalline silicon (nc-Si:H) formation [1]. There are several reports in the literature that provide conflicting suggestions about the structure of a p-type materials deposited under similar conditions [2, 3]. It is important to understand the exact nanostructure of the p-type material used at UT and other laboratories to produce high-Voc solar cells. Unfortunately, it is challenging to obtain results that lead to a definite conclusion since on one hand, the p-layer Si:H material, ~15nm thick, is deposited on an a-Si substrate in an a-Si n-i-p type solar cell and the commonly used methods to determine the nanostructure of these materials require the films to be at least 100nm in thickness and are deposited on glass or crystalline Si substrates while on the other hand, the nanostructure of the thin film Si:H based material depends sensitively on the substrates and the thickness in addition to the deposition conditions such as hydrogen dilution and substrate temperature. In an earlier paper, we reported our preliminary finding that these p-type materials used in UT's high-Voc solar cells are fine-grained nc-Si:H, based on a modeling study using AMPS [4]. In this paper, we report our further investigation of the nanostructure of this p-type material using High Resolution Transmission Electron Microscope (HRTEM), which allows us to directly measure the nanostructure of the films, ~15nm thick, deposited on a-Si substrates.

Experimental

A-Si:H solar cells are deposited using RF-PECVD on stainless steel covered with an Al/ZnO back reflector. The n- and i-layers are deposited under the conditions reported earlier [1] and these are the same conditions used in the fabrication of high-efficiency triple-junction solar cells at UT [5]. These p-layers are deposited using a high hydrogen dilution, high rf power, and a low substrate temperature, and with a seed layer to promote nanocrystalline Si:H formation.

Raman scattering is performed to characterize the structure of films. The 488-nm laser line from a water-cooled Ar+ laser is used for the excitation. The samples used for Raman study are approximately 350 nm thick and are deposited on glass substrates. Optical transmission is also measured for these samples. Raman spectra are measured from both the front side of the films as well as the back side of films through the glass substrates.

For HRTEM, a Jeol 2010 STEM microscope is used. The samples for the HRTEM study are 15nm-thick boron-doped p-layer deposited on a 15nm-thick intrinsic a-Si:H layer that is grown under the same conditions as the intrinsic layer in a high-Voc a-Si:H solar cell. The Si:H layers, with a combined thickness of 30nm, are first deposited on a glass substrate and then peeled off from the substrates using diluted hydrofluoride acid for the HRTEM measurement.

Results and Discussions

Figure 1(a) shows the Raman spectrum of a 350 nm thick p-layer deposited on a glass substrate. The spectrum is deconvoluted into three major peaks, located at 480cm^{-1}, 514 cm^{-1} and around 500cm^{-1}, corresponding to the amorphous phase, the nanocrystalline phase and the grain boundary interfaces, respectively. According a bond polarizability model [6], a 514cm^{-1} Raman peak corresponds to a nc-Si with mean nanocrystalline grain size of approximately 2.1 nm. We believe that the actual grain size may be larger than this value since the phonon confinement effect may be overestimated in using this model without considering the existence of tensile stress in the film.[7]

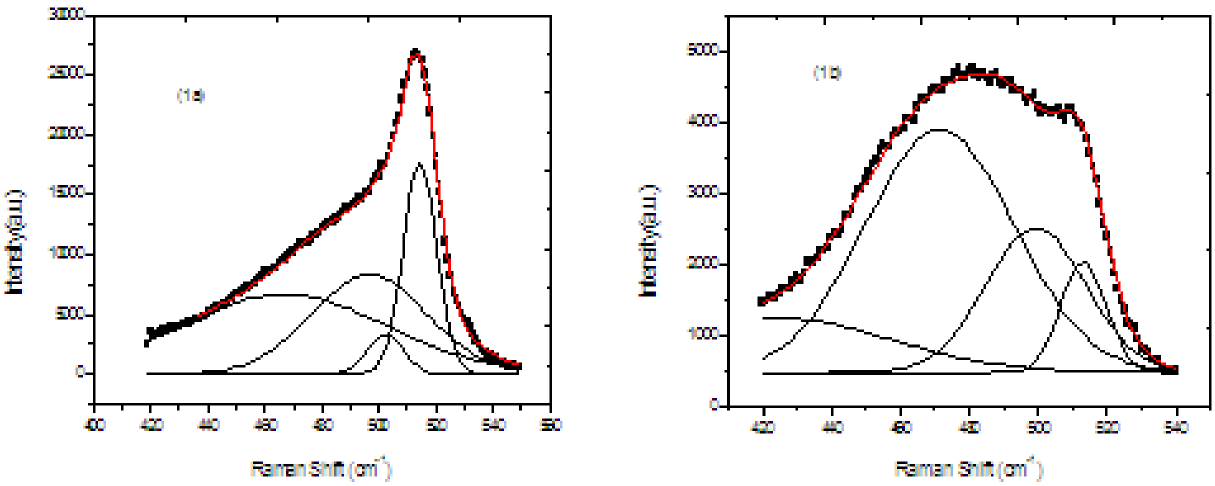

Fig.1 The Raman spectra taken from the front side surface (1a) and the back side (1b) of the p-layer through the glass substrate.

Since the 350nm sample is thicker than the 15nm layer used in an actual solar cell, the nanostructure of the sublayer probed by Raman may have higher volume fraction of nanocrystalline phase than the initial 15nm deposited on the substrate. To effectively measure the nanostructure of the film initially deposited on the substrate, we measured Raman spectra also from the back side of the sample, through the glass substrate. The results are shown in Figure 1b. Raman spectrum taken through the glass substrate shows a smaller crystalline volume fraction. However, the deconvoluted peaks still shows a 514cm-1 Raman scattering peak, indicating the existence of fine-grained nc-Si during the initial growth of the film when it is deposited on glass.

One may still question the results from Raman spectrum obtained through the glass substrate because 1) at 488nm laser line, the Raman scattering may be from the sublayer of the film that is up to 100 nm thick which corresponds to the absorption depth for this laser line; and 2) the initial film is deposited on glass and therefore may have different nanostructure than those films deposited on a-Si substrate as in an n-i-p type solar cell.

In order to characterize the thin p-layer in a solar cell, HRTEM was performed on a 15-nm thick p-layer (Sample A) grown on a 15-nm intrinsic a-Si:H layer, which was deposited under identical conditions as those used in solar cells. Figure 2a shows a high-angle annular dark-field (HAADF) image, exhibiting many separated bright dots which are characteristics of nanocrystalline Si. Most of these bright dots, the nc-Si:H grains, have a size of around 3 to 5 nm, which is larger than the size estimated from Raman measurement. Figure 2a also shows that several large white dots are the clusters of 3 or 4 crystalline grains. Figure 2b is the selected-area electron diffraction (SAED), showing a diffraction pattern with crystalline feature for the area probed.

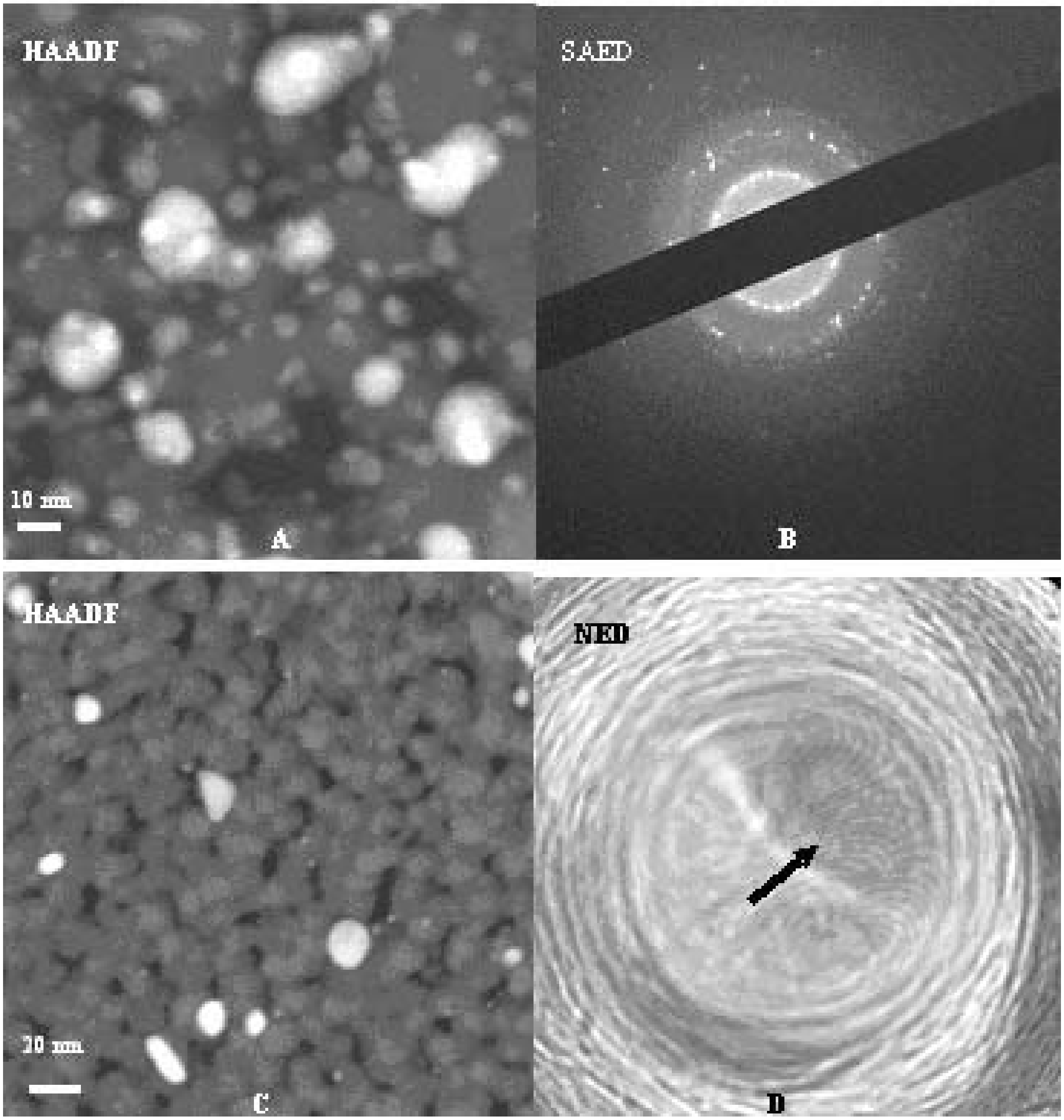

Figure 2a and 2b are HAADF and SAED images of the Sample A with a seed layer between the p-and i-layer; Figurs 2c and 2d are HAADF and NED images of the Sample B which has a slightly less Voc.

We deposited another p-layer (Sample B) on a-Si under the same conditions described above but without the seed layer that promotes nc-Si growth. Such a p-layer usually leads to an a-Si:H solar cell with approximately 20mV less in Voc. Figure 2c shows a HAADF image of Sample B, exhibiting smaller volume fraction of nanocrystalline grains. In order to show that these white dots on Samples A and B are indeed nanocrystalline grains, nano-electron diffraction (NED) was measured for one of the bright dots in Fig. 2c (a grain in Sample B) and the result is shown in Fig. 2d. The interference fringes near the center indicate the white dots correspond to crystalline structure. Comparing the HAADF images of Samples A and B shown in Figures 2a and 2b, respectively, it is concluded that a p-layer material with higher volume fraction of nc-Si:H phase leads to a higher Voc in an a-Si n-i-p type solar cell.

Another p-layer, Sample C, was deposited under a similar condition as Sample A but with higher rf power. Raman spectrum measured from both the front and backside on glass shows that this p-layer material is amorphous without any observable nc-Si:H phase. When this p-type material is used in an nip a-Si:H solar cell, it leads to a Voc of 0.98V, less than the p-type materials that contains fine-grained nc-Si:H.

A-Si:H nip solar cells, incorporating above-described nc-Si:H p-layers, are fabricated on stainless steel substrates coated with a Al/ZnO back reflector. The solar cells fabricated using Sample A deposition conditions for the p-layer show an average Voc of 1.040 V. The cells with the highest performance show a Voc of 1.042 V, a fill factor of 0.734, a short circuit current of 11.6 mA/cm2, and an efficiency of 10.03 %.

Conclusion

The p-layer used at UT to obtain high-Voc a-Si solar cells is a mixed–phase material that contains nc-Si:H grains, ~3-5 nm in size, embedded in an a-Si:H matrix. Comparing HAADF images of two samples (Samples A and B), it is concluded that the mixed phase p-layer with a higher volume fraction of nc-Si:H phase, within the range studied, leads to a higher V_{oc}. The optimum p-layer material for nip-type a-Si:H solar cells is neither at the onset of the transition between amorphous to (amorphous and nanocrystalline) mixed phase nor a nanocrystalline/microcrystalline material with a high volume fraction of crystalline phase.

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